Microstructures of Porous NiTi Alloy Prepared by Transient Liquid Phase Diffusion Synthesizing Process

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Abstract

Porous NiTi alloys are potential functional structural materials; however, the properties of porous NiTi alloys are not avalible for practical use as there are not desirable fabricating methods at present. This paper has provide a new way for fabricating porous NiTi, namely, transient liquid phase synthesizing process with the powder mixture of NiTi2 and Ni as raw materials. The results show that a porous NiTi alloy, with porosity of around 10% and pore size of within 20 μ m, is obtained when the (NiTi2+Ni) green sample is heated above 1000 ^{o}C for 30 min. The metal wall of porous NiTi alloy has a NiTi phase dominant microstructure with a few granular shaped second phases of NiTi2 and Ni3Ti. Both the pore shape and second phase shape get much round with increasing synthesizing temperature and time. The synthesizing procedure and its mechanism have been discussed.

Keywords

X-ray Diffraction; Shape Memory Alloys; Porous Materials; Powder Technology; Transient Liquid Phase Diffusion

Introduction

Porous NiTi is attractive for biomedical applications because of its shape memory effect, super elasticity, good biocompatibility as well as Young`s modulus similar to human hard tissues [1,2]. Porous NiTi has been fabricated based on powder metallurgy [3] with or without space-holders [4, 5]. Many of these solid-phase sintering processes result in poor densification of the NiTi powders into walls due to the low sintering ability. Bansiddhi and Dunand [6,7] showed that transient liquid phase sintering can be performed on preparation of porous NiTi-Nb alloy which exhibited the same shape memory effect as porous NiTi SMAs. However, this method need a high temperature and a long time, and moreover it cannot fabricate Ni-Ti binary alloy as it is based on NiTi-Nb eutectic liquid at 1185^{o}C. NiTi2 is a low melting point phase and can be used in liquid phase sintering process. In this paper a powder mixture of NiTi2 and Ni with equiatomic Ni/Ti ratio were sintered at a temperature slight higher than that of NiTi2`s melting point (984^{o}C) and a porous NiTi alloy was fabricated through the diffusion of atoms between NiTi2 liquid phase and Ni powders.

Experimental

Two types of metallic powders were used as raw materials: NiTi2 (99%purity, 61~74μm, self-made) and Ni (99%purity, 30~38μm, commercially obtained). Powder compacts were made by encasing powder mixture of equal Ni/Ti ratio into cylindrical ingots of 16 mm in diameter and 8mm in height and pressing it at a pressure of 200MPa. The green sample was sealed with a vacuum quartz tube which was evacuated to a base pressure of about 8×10^{-5}mbar. Sintering process was carried out in a furnace by heating to 1000^{o}C or 1050^{o}C for a time span of 30~120minutes, followed by water quenching a the room temperature.

Cross sections of the synthesized specimens were mounted in epoxy resin, polished with SiC paper and diamond paste, and imaged with an optical microscopy (Leica DMR) and SEM (LEO-1450) equipped with an energy dispersive spectrometer (EDS). Phase constituents were determined by X-Ray Diffractometer (XRD, D/Max- RB 12KW).

Results

Phase Constitutions

FIG.1 shows the XRD spectra of synthesized NiTi specimens sintered at 1000^{o}C and 1050^{o}C, respectively. In both spectra, four phases can be found, namely NiTi (B2), NiTi (B19`), Ni3Ti and NiTi2 phase. NiTi (B2) phase is the dominating phase. To contrast FIG.1(b)

with FIG.1(a), NiTi (B2) phase shows a relatively high and narrow peak, which indicates more NiTi (B2) phase has been formed at high temperature synthesizing process.

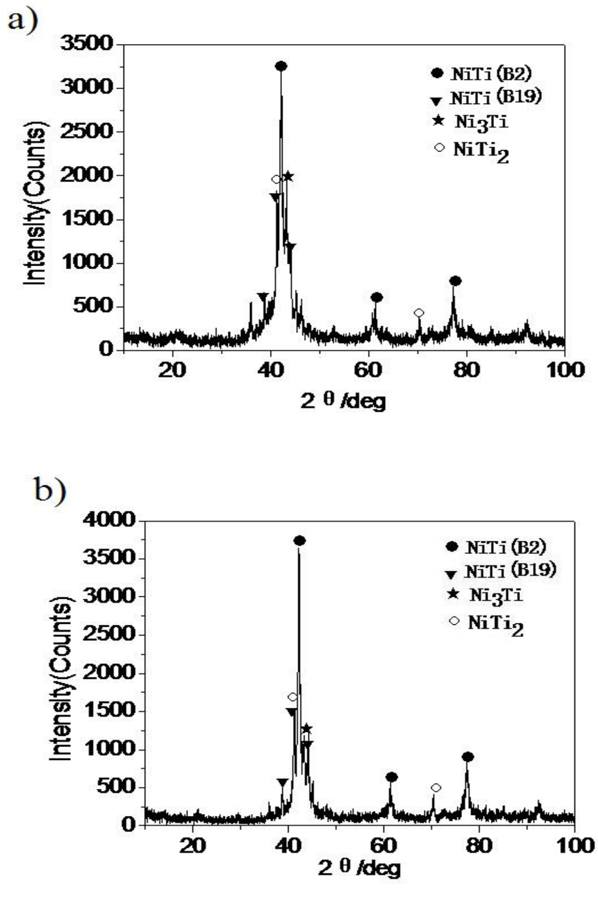

FIG. 1 XRD SPECTRA OF POROUS NITI SYNTHESIZED AT

a) 1000°C - 60MIN OR b) 1050°C -60MIN

Macrostructures

Macrostructures of synthesized NiTi specimens are shown in FIG.2 One can find that the samples are the porous structures with a homogeneous distribution of pores.

The porosity is around 10% and the pore size is within 20μm. The pore shape at high temperature sintered samples is much rounder than that of low-temperature sintered sample. According to the Ni-Ti binary phase diagram, the composition range of liquid phase increases with temperature ascending, which means more Ni atoms can be dissolved into the liquid NiTi2 phase. Therefore, at a higher sintering temperature, both the liquid phase amount and its existing time increase and the modulation of the liquid phase on pore walls will strengthen to make pore shape more round and smooth.

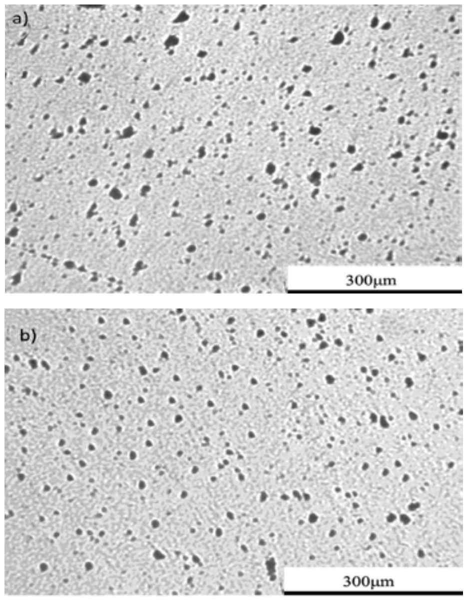

FIG. 2 OPTICAL MOCROGRAPHY OF POROUS NITI SYNTHESIZED AT a) 1000°C -60 MIN OR b) 1050°C -60MIN

Microstructures.

In the SEM micrographs (see FIG.3) of synthesized NiTi one can find three color phases, namely, gray matrix, light phase and dark phases, respectively.

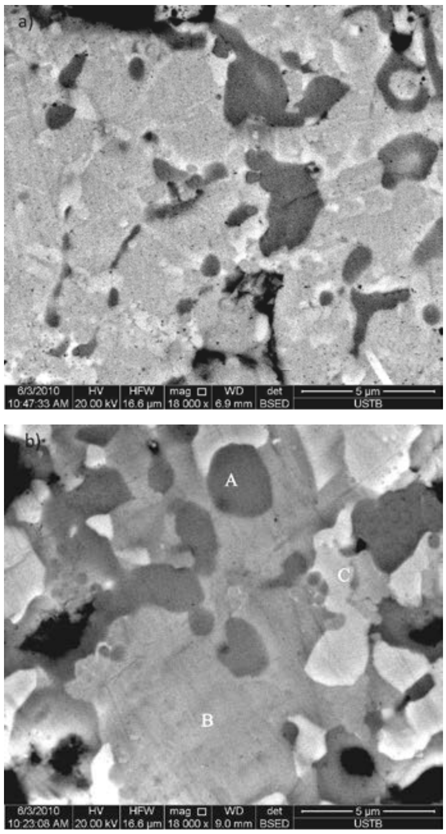

FIG. 3 SEM MICROGRAPH OF POROUS NITI SYNTHESIZED AT

a) 1000°C - 60MIN OR b) 1050°C -60MIN

In the microstructures of synthesized NiTi alloy, light phases and dark phases are netted distributed. While

in those of 1050°C lasting for 30min synthesized one, the light phases and dark phases are granular shaped with the size less than 2μm.

EDS analysis results (as shown in TABLE 1) show that the Ni/Ti ratio of the gray matrix is close to 1, while the ratios of light phase and dark phase are close to 3 and 1/2, respectively. Combining EDS analysis results with XRD spectra, the gray matrix phase can be defined as TiNi (from either the B2 phase or B19` phase), light phase as Ni3Ti and dark phase as NiTi2, respectively.

TABLE 1 EDS ANALYSIS OF PHASES IN SYNTHESIZED NITI (AT%)

Phases	1000°C -60min		1050°C -60min	
	Ti	Ni	Ti	Ni
Matrix	48.79	51.21	49.01	50.99
Dark	66.37	33.63	64.97	35.03
Light	25.28	74.72	28.58	71.42

Discussions

The liquid phase diffusion synthesizing process will begin when the green sample is heated to a temperature higher than the melting point (984°C) of NiTi2 phase. The synthesizing procedure can be described as: (1) NiTi2 powders melt into liquid phase; (2) liquid phase spread out on surface of Ni particles; (3) atoms migrate between solid/liquid interface, mostly Ti atom migrates from liquid to solid and Ni atom migrates from solid to liquid; (4) NiTi phase coagulates in the liquid side due to isothermal solidification reaction as the nickel concentration of the liquid phase surpasses certain amount; (5) meanwhile, Ni3Ti phase forms in solid Ni side due to combination reaction as titanium concentration of the Ni phase at a certain amount; and (6) NiTi phase grows and the raw materials of NiTi2 and Ni decline continuously by step (3) to step (5) repeat along with heating time.

As mentioned above, liquid phase synthesizing reaction is not only a simple physical diffusion process but also a chemical diffusion process. The whole process progress is comprised of atomic diffusion and combination reaction, and is governed by the diffusion rate. According to the second law of thermodynamics, spontaneous process proceeds towards the reduction of Gibbs free energy (GFE) of whole system. The occurrence of following combination reaction will depend on the relative amount of GFEs of the participation phases in reaction at the sintering temperature.

NiTi2 (l)+Ni(s)

→NiTi2 (l)+ NiTi(s) +(NiTi(s) +Ni3Ti(s))+Ni(s)

→Ti2Ni(l)+ NiTi(s) +(NiTi(s) +Ni3Ti(s))

→Ti2Ni(s)+ NiTi(s) +Ni3Ti(s)

The temperature dependence of GFEs of binary intermetallic compounds of NiTi, NiTi2 and Ni3Ti is shown in FIG. 4. It can be found that GFEs of all of them decrease with the increase in temperature. However, GFE of NiTi phase is the highest among them. It implies that a certain amount of residual NiTi2 and Ni3Ti phase would always exist when NiTi alloys are prepared by this transient liquid phase synthesizing process.

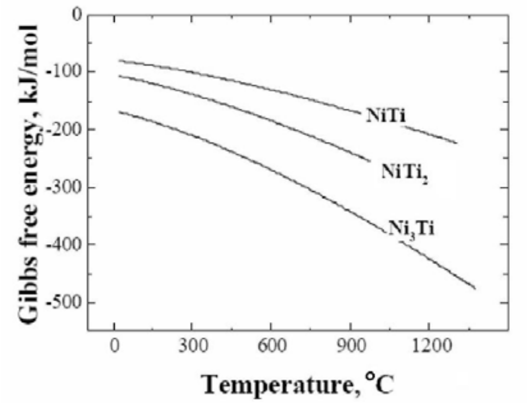

FIG. 4 GIBBS FREE ENERGY VS. TEMPERATURE CURVES FOR NITI, NITI2 AND NI3TI PHASES

Conclusions

1) Porous TiNi alloys can be prepared when the powsers mixture compact of Ti2Ni and Ni is heated at a temperature above 1000°C and lasting for 30 minutes.

2) The synthesized porous NiTi alloy mainly consists of NiTi matrix phase (B2 and B19`) and few Ti2Ni, Ni3Ti phases.

3) With synthesizing temperature increasing, the pore shape and the shapes of NiTi2, Ni3Ti phases tend to round.

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Xingke Zhao, born in China in September 1966, majored in welding techniques and graduated from South China University of Science and Technology (Guangdong province, China) in 1988., and received his Ph.D in Materials Science and Engineering at the Harbin Institute of Technology. University (Heilongjiang province, China) in 2002.

He currently lectures the undergraduate and graduate, meanwhile, leading relevant researches, in the materials welding and joining techniques courses. His research concerning with ferrous alloys (carbon steel, stainless steel and Fe-Ni alloy) and non-ferrous alloy (Ni-Ti alloy). In recent years his research interests mainly focus on powder metallurgical reaction kinetics of (Ti_2Ni+Ni) system, which can be used to fabricate porous NiTi alloys as well as to assemble NiTi materials in similar joints.

Xiang Gao is a post-graduated researcher involved in development of fabricating porous NiTi alloys by Partial Transient Liquid Phase Diffusion techniques.